REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 074-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including g the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of the collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 4 May 2007	3. REPORT TYPE AND DATE COVERED

4. TITLE AND SUBTITLE
Dielectric studies in materials for high energy density capacitors

Turo, Andrew J.

5. FUNDING NUMBERS

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

US Naval Academy
Annapolis, MD 21402

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

Trident Scholar project report no. 360 (2007)

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
This document has been approved for public release; its distribution is UNLIMITED.

12b. DISTRIBUTION CODE

13. ABSTRACT The energy requirements of technologies today are more demanding than ever. The requirement for large energy storage and a quick release of that energy is becoming a greater and greater problem. Limited by size, cost, and the speed of chemical reactions, batteries need to be replaced as a primary source of stored energy. Capacitors have the ability to perform in many of the areas where batteries and other energy sources fall short. One way to increase the performance of a capacitor is by inserting a dielectric material. The dielectrics polypropylene and Ultem® were the focus of this study, polypropylene as a control and Ultem® due to its ability to handle high temperatures, structural stability, and good dielectric characteristics. Ultem® was studied in both its pure form and with the addition of mesoporous silica, which theoretically should lead to an increase in dielectric performance while maintaining structural stability. This was done through the casting of Ultem® films which underwent dielectric breakdown testing and broadband dielectric spectroscopy. Broadband dielectric spectroscopy analyzed the AC voltage and current relationship in materials at different frequencies and temperatures. The data produced allowed the calculation of the dielectric constant and loss and gives insight into these values. Dielectric strength measurement is a new experiment at the Naval Academy, so part of this project was to develop the methods to be used. This involved developing sample preparation techniques, voltage ramping procedures, and validations of the test equipment. Results confirm the

14. SUBJECT TERMS
LISA, satellite, formation, insertion error

15. NUMBER OF PAGES
53

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

	Form Approved OMB No. 074-0188
REPORT DOCUMENTATION PAGE	

Public reporting burden for this collection of information is estimated to average 1 hour per response, including g the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of the collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 4 May 2007	3. REPORT TYPE AND DATE COVERED	

4. TITLE AND SUBTITLE
Dielectric studies in materials for high energy density capacitors

Turo, Andrew J.

5. FUNDING NUMBERS

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
US Naval Academy
Annapolis, MD 21402

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
Trident Scholar project report no. 361 (2007)

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
This document has been approved for public release; its distribution is UNLIMITED.

12b. DISTRIBUTION CODE

13. ABSTRACT (cont) This, however, was extremely dependant on the thickness of the material tested. Mesoporous silica was added to the Ultem® in an effort to improve breakdown strength. However, when mesoporous silica was added to cast samples, the samples become brittle and had a drop in the breakdown strength. These samples were tested using X-ray Diffractometry, which gave no evidence of crystallization in samples with mesoporous silica. Broadband dielectric spectroscopy measurements show that pure solution cast Ultem® is similar to commercially produced Ultem®, especially with respect to a water dielectric loss peak between 220-230K. The addition of mesoporous silica coated with polystyrene created an additional loss peak at low temperatures, around 150K, and overlapping the low temperature water loss peak. Neither of these peaks were noticed in "dry" Ultem® without nanoparticles. At high temperatures, especially around the glass transition temperature, the addition of nanoparticles had no effect upon Ultem's® dielectric loss.

14. SUBJECT TERMS
Dielectric breakdown, dielectric spectroscopy, high energy density capacitors, Ultem®

15. NUMBER OF PAGES 53
16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

DIELECTRIC STUDIES IN MATERIALS FOR
HIGH ENERGY DENSITY CAPACITORS

by

Midshipman 1/c Andrew J. Turo
United States Naval Academy
Annapolis, Maryland

_____
(signature)

Certification of Adviser Approval

Associate Professor Charles A. Edmondson
Physics Department

_____
(signature)
_____
(date)

Acceptance for the Trident Scholar Committee

Professor Joyce E. Shade
Deputy Director of Research & Scholarship

_____
(signature)
_____
(date)

USNA-1531-2

Abstract

The energy requirements of technologies today are more demanding than ever. The requirement for large energy storage and a quick release of that energy is becoming a greater and greater problem. Limited by size, cost, and the speed of chemical reactions, batteries need to be replaced as a primary source of stored energy. Capacitors have the ability to perform in many of the areas where batteries and other energy sources fall short.

One way to increase the performance of a capacitor is by inserting a dielectric material. The dielectrics polypropylene and Ultem® were the focus of this study, polypropylene as a control and Ultem® due to its ability to handle high temperatures, structural stability, and good dielectric characteristics. Ultem® was studied in both its pure form and with the addition of mesoporous silica, which theoretically should lead to an increase in dielectric performance while maintaining structural stability. This was done through the casting of Ultem® films which underwent dielectric breakdown testing and broadband dielectric spectroscopy.

Broadband dielectric spectroscopy analyzed the AC voltage and current relationship in materials at different frequencies and temperatures. The data produced allowed the calculation of the dielectric constant and loss and gives insight into these values. Dielectric strength measurement is a new experiment at the Naval Academy, so part of this project was to develop the methods to be used. This involved developing sample preparation techniques, voltage ramping procedures, and validations of the test equipment.

Results confirm the developed dielectric breakdown technique by the study of polypropylene. Solution cast Ultem® was produced and studied showing similar results to commercially produced materials, yielding a breakdown strength of 12,010 V/mil and an energy density of 3.17 J/cc. This, however, was extremely dependant on the thickness of the material tested. Mesoporous silica was added to the Ultem® in an effort to improve breakdown strength. However, when mesoporous silica was added to cast samples, the samples become brittle and had a drop in the breakdown strength. These samples were tested using X-ray Diffractometry, which gave no evidence of crystallization in samples with mesoporous silica.

Broadband dielectric spectroscopy measurements show that pure solution cast Ultem® is similar to commercially produced Ultem®, especially with respect to a water dielectric loss peak between 220-230K. The addition of mesoporous silica coated with polystyrene created an additional loss peak at low temperatures, around 150K, and overlapping the low temperature water loss peak. Neither of these peaks were noticed in "dry" Ultem® without nanoparticles. At high temperatures, especially around the glass transition temperature, the addition of nanoparticles had no effect upon Ultem's® dielectric loss.

Keywords:

Dielectric Breakdown

Dielectric Spectroscopy

High Energy Density Capacitors

Ultem®

Acknowledgements

I would like to thank all those who assisted and collaborated with me on this project: Professor John Fontanella for assisting me with the dielectric spectroscopy, Professor Joseph Lomax for providing the nanoparticles, and the Physics Machine Shops for building the mask used.

I am also grateful for the assistance of Professors Craig Whitaker and Arthur Rachwald and CDR Mark Larabee, USN, in serving as my Trident Committee Guides, as well as Professor Joyce Shade for her intimate involvement as the Committee Chair.

I would also like to thank the Office of Naval Research for the grant given to the Naval Academy for dielectrics research.

Thanks and love to my parents, for putting up with me and pushing me to my limits. Without your eternal support I would not have accomplished all I have.

Finally, I would like to thank Professor and Mrs. Charles Edmondson. Their support and hospitality have made this experience as valuable and successful as possible.

Table of Contents

List of Figures

List of Equations

I. Introduction

The use of capacitors is of basic interest to the Navy and the United States. Many technologies currently under development will employ capacitors. For example, rail guns, electromagnetic launchers on aircraft carriers, and back-up power generators are all technologies in which capacitors play an integral part. Their success depends in part on the improvement of state-of-the-art capacitors.

Capacitors have two significant properties that we wish to understand and harness for practical usage: the ability to store large amounts of energy and the ability to release energy quickly. Batteries are inadequate in these applications, because they release energy based on a chemical reaction. This limits the amount of energy they can store and the rate at which it can be released. Thus, our ability to increase the performance of capacitors with regard to the factors of cost and size is of tremendous interest.

The Office of Naval Research (ONR) has compiled a team of researchers to attack several problems involved with building a high energy density capacitor for naval usage. All aspects of the capacitor system from electrode to dielectric are being studied. As part of the ONR research initiative, this project focuses on the properties of the dielectric materials to be used within the capacitors, specifically the dielectric strength, constant, and loss. We chose to study Ultem®, a polyetherimide developed by General Electric. Ultem® is a good candidate material because of its mechanical durability and good dielectric properties. The Ultem® was solution cast, and results were compared to commercially available Ultem® sheets. Following a technique that has a shown promise in polypropylene, nano-particles, in the form of mesoporous silica, were added to the solution cast Ultem® to determine the resulting effects on Ultem's® dielectric and mechanical properties.

II. Background Information

A. Capacitors

A capacitor is a device that stores energy. The most basic of these can be thought of as two parallel conductive plates in vacuum. When equal but opposite charges are put on these plates, they create an electric field in which energy is stored. We define the capacitance, C, as the ratio of the charge, Q, to the potential difference, V:

$$C \equiv \frac{Q}{V} \qquad\qquad \text{Eq. 1}$$

In the basic capacitor, where there are two parallel conductive plates as shown in Figure 1, we find that the electric field between these plates is approximately uniform.

Figure 1: Basic Capacitor

Gauss' Law can be used to show that in a parallel plate capacitor the magnitude of electric field is $\left| \vec{E}_o \right| = \dfrac{\sigma}{\varepsilon_0}$, where σ is the surface charge density on the electrodes and ε_0 is a constant called the permittivity of free space. From this we can draw a potential difference relationship:

$$V = E_o d = \frac{Q_o d}{A \varepsilon_o} \qquad\qquad \text{Eq. 2}$$

Substituting this into Equation 1 we find:

$$C_o = \frac{Q_o}{V} = \frac{\varepsilon_0 A}{d} \qquad\qquad \text{Eq. 3}$$

Where A is the surface area of the plates of the capacitor and d is the distance between them.

When a dielectric is placed between the two plates of a capacitor, it increases the capacitance of the capacitor by a factor of ε'. This factor is called the dielectric constant and is unique to each dielectric material.

$$C = \varepsilon' C_0 \qquad\qquad \text{Eq. 4}$$

The reason for this is of interest to us. When a potential difference is placed on the plates of a capacitor it forms an electric field. When a dielectric is placed between the plates it polarizes the molecules which create surface charge on the plates of the capacitor. Figure 2 shows how these charges form their own electric field $\vec{E}_d$ (orange), which opposes the original electric field $\vec{E}_o$ (black). The resultant or total electric field is smaller than the original electric field $\vec{E} = \vec{E}_o - \vec{E}_d$.
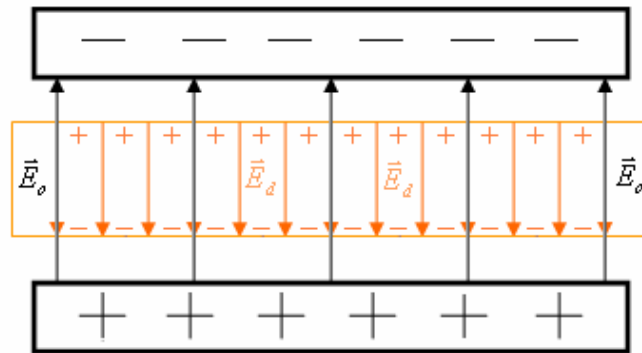

Figure 2: Fields in a Capacitor With a Dielectric

This reduction of the field allows more charge to be added to the plates for a given applied potential. The ratio between the field created without the dielectric and the resultant field when the dielectric is present also defines the dielectric constant:

$$\varepsilon' \equiv \frac{E_0}{E}$$ Eq. 5

From this definition and by using Equations 1 and 2 we find an alternate form for capacitance:

$$C = \frac{\varepsilon' \varepsilon_0 A}{d}$$ Eq. 6

As stated above, we defined $C = \frac{Q}{V}$ thus $V = \frac{Q}{C}$. We also know from the definition of potential $V = \frac{\partial U}{\partial Q}$, or the change in potential energy, U, with respect to charge. Thus, using Leibniz notation and substituting for V we find $\partial U = \frac{Q}{C} \partial Q$. By integrating both sides we see $U = \frac{Q^2}{2C}$. By substitution of $Q = CV$ we also see that:

$$U = \frac{QV}{2} = \frac{CV^2}{2}$$ Eq. 7

From this we see that the capacitance has a linear relationship to stored energy, and if we can raise capacitance we can increase the amount of energy our capacitor can store. Also, the energy varies as the square of the voltage.

By substituting Equations 1 and 4 into Equation 5 we find:

$$U = \frac{CV^2}{2} = \frac{1}{2}\left(\frac{\varepsilon_0 A}{d}\right)(Ed)^2 = \frac{1}{2}\varepsilon' \varepsilon_0 E^2 (Ad)$$ Eq. 8

From this we reaffirm that by changing the dimensions, (Ad), of the capacitor we can store more energy in it. However, it also gives us insight into the importance of the magnitude of the electric field to the energy stored by a capacitor, showing that the field is a squared term.

Next, (Ad) is the volume of space between the capacitor plates. Thus we define u_e as the energy density or $\dfrac{energy}{volume}$.

$$u_e \equiv \frac{1}{2}\varepsilon'\varepsilon_0 E^2 \qquad\qquad \text{Eq. 9}$$

The energy density of a capacitor is an important quantity. It represents one factor of the performance of a capacitor that we can control without changing the dimensions of the capacitor. Our equation for energy density has two variable inputs: the dielectric constant and the electric field across the dielectric material, which at its maximum value is called the dielectric strength. Therefore, in order to create the best performing dielectric for any given size and shape, we need to maximize either the dielectric constant of the material, the dielectric strength, or both.

The final property which needs to be taken into consideration when examining the performance of a dielectric is called dielectric loss. Dielectric loss results from the fact that during a changing field across a dielectric, some of the energy is lost via conductivity or a relaxation process. The loss due to a relaxation process results in lost energy during the polarization of the dielectric. One way of quantifying dielectric loss is by defining a complex dielectric constant:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \qquad\qquad \text{Eq. 10}$$

Using this form of the dielectric constant we can define a complex capacitance as:

$$C^* = C - i\frac{G}{\omega} \qquad\qquad \text{Eq. 11}$$

where G is the conductance (reciprocal of the resistance) and ω is the angular frequency of the AC signal applied. Using a similar form as Equation 7, we define conductance as:

$$G = \frac{\varepsilon_0 \varepsilon'' \omega A}{d} \qquad \text{Eq. 12}$$

We can also define the electrical conductivity, σ, of a material as:

$$\sigma = \varepsilon_0 \varepsilon'' \omega \qquad \text{Eq. 13}$$

This shows that the imaginary part of the dielectric constant is related to the electrical conductivity of a dielectric.

B. Dielectric Strength and Measurements

As stated above, dielectric strength is the maximum electric field which a dielectric can withstand before it breaks down, or fails. According to Costa et al., the breakdown measurements are usually done in one of two ways, as either "the charge-to-breakdown Q_{BD}, defined as the time-integrated current density which flows until breakdown occurs, [or] the time-to-breakdown t_{bd}, defined as the sample's lifetime."[1] The charge-to-breakdown measurements are done by attaching two electrodes to the sample and ramping up a potential across the sample until failure occurs. Lifetime measurements are done by placing a voltage on a sample and recording how long it takes for breakdown to occur. For the purpose of this study, only charge-to-breakdown measurements were used.

The leading theory as to why breakdown occurs in dielectrics has to do with defects. Irene states that there are four types of defects defined by the dimension they effect: point (0-D), line (1-D), planar (2-D), and bulk (3-D). Each defect is due to the break of a chemical bond and the consequent rise of free energy, at least in a perfect crystal.[2] Even though Ultem® is amorphous, the idea of free charge and broken bonds can still be used to explain their defects.

While defects may be assumed to be the cause of dielectric breakdown, it is understood that there are four mechanisms for breakdown: electrical, discharge, electromechanical, and thermal runaway. In the electrical mechanism, an atom ionizes, creating a free charge. This free charge can be viewed as a free electron liberated by the defects within the polymer. The release of this electron may be due to impurities, such as carbon fiber, nylon, copper, or aluminum as was noted to exist in polymer insulation[3], or defects in the structure. The free electron accelerates in the electric field. As it does so, it collides with other atoms creating secondary ionizations within the polymer, which in turn do the same. This cascading effect ends up in the continuous movement of electrons, or a charge moving through the material. The current cuts a path through the polymer, turning a capacitor into a conductor. This is defined as breakdown.

In the discharge mechanism, voids are the primary cause of breakdown. Within a void, free electrons are allowed to be excited by the applied electric field. As opposed to the electrical mechanism, these electrons do not cascade, but rather deteriorate the sides of the void in which they are contained. This allows the release of atoms bordering the void, increasing the size of the void until either the material is completely degraded or until an electron can ionize and cascade across this weakened section of the material, causing breakdown.

Due to these mechanisms of breakdown, we identify several factors that must be considered when studying the breakdown phenomenon. First, since it is primarily due to defects and voids within the material, whether intrinsic to the material or artificial, it will always exist. Even as production processes become cleaner and polymers more pure, dielectric strength will always need to be considered.

Second, in order to reduce the breakdown effect we must attack the defects, free charges, and intrinsic properties of the material. There are two main ways to do this: mechanically and

chemically. Mechanically applies to the production process. Defects are usually added during production. Significant reduction in defects can often be achieved by changing the production process. Chemically means adjusting the polymer on the chemical level to deal with free charge or the properties of the material either with chemical alteration or the addition of filler materials. Some of the most promising filler materials are nanoparticles, which will be discussed later.

There are two other mechanisms which also affect how and when breakdown occurs within a material: thermal runaway and electromechanical. Since temperature can be defined as a measure of the internal energy of a system, as we increase the temperature of a material, the average energy of the atoms within the material increases.[4] Therefore, as the temperature increases, the atoms become more excited allowing a greater response to the applied electric field. This leads to greater losses, which leads to more thermal energy. All the while, as the temperature increases, the energy of the outer electrons of atoms within the material are closer to ionization energies, making it is easier for breakdown to occur.

The electromechanical mechanism is related to a more intrinsic property of the material. As amorphous polymer materials are heated they transition through what is known as a glass transition temperature, T_g. At T_g, the material experiences a shift from a brittle "glassy" phase to a softer "rubbery" phase. Above this temperature, the material looses its rigidity, and is able to be compressed more easily. Therefore, in a capacitor, the two oppositely charged electrodes are attracted to each other and compress the softer material. The decrease in distance between the electrodes increases the electric field, leading to breakdown.

C. Broadband Dielectric Spectroscopy

In order to study the dielectric constant and loss the materials we used a technique called dielectric spectroscopy. This is done by using an impedance bridge which applies an AC voltage across a sample over a broad range of frequencies and measures the resulting response.

From Ohm's Law we can derive the equations necessary to understand the basics of complex impedance:

Ohm's Law for DC $\quad\quad\quad\quad V = IR$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ Eq. 14

Ohm's Law for AC $\quad\quad\quad\quad V(\omega,t) = I(\omega,t)Z(\omega)*$ $\quad\quad\quad\quad\quad\quad$ Eq. 15

Where the Complex Impedance, $Z(\omega)*$, is defined as:

$$Z*(\omega) = Z'(\omega) + iZ''(\omega) \quad\quad\quad\quad\quad\quad \text{Eq.16}$$

In a given circuit, V is the voltage, I is the current, and R is the resistance. Z' is the real part of the impedance, and Z'' is the imaginary part multiplied by i the imaginary constant, the square root of negative one. The Andeen Capacitance Bridge Model CGA-83 determines these values by applying an AC voltage and analyzing the sample as a complex capacitor and reporting the results as capacitance and conductance over the angular frequency ($\frac{G}{\omega}$). The response of the dielectric to the AC field is governed by a process called dielectric relaxation, and this often allows us to understand the microscopic properties of a material.[5]

For dielectric relaxation, an AC voltage applying an alternating electric field drives a system of dipoles. The observed loss peaks provide information about the responses of the material. Due to the bonds within the material, there is a lag, or phase shift, between the applied field and the materials reaction, or polarization. This lag causes losses in the material, normally dissipating into the environment through heat. Since this energy is lost to the environment is lost,

as opposed to being stored in polarization, reduction of this relaxation loss peaks of the material are a key to improving polymer dielectrics.

D. Ultem[®]

Ultem[®] is a polyetherimide originally produced by General Electric under US Patent 5,357,033. It is a desirable dielectric for several reasons, including its mechanical durability, ease of mass production, and relatively high dielectric constant. There are also some properties of Ultem[®] which should be noted due to the interesting effects they have upon its dielectric performance. Figure 3 shows the chemical make up of a single Ultem[®] 1000 monomer, the most common form of the polymer. There are polarizable benzene groups at the end of the monomer. This allows the molecule to polarize when placed in an electric field, giving it good dielectric properties including a theoretical energy density of 7 J/cc.
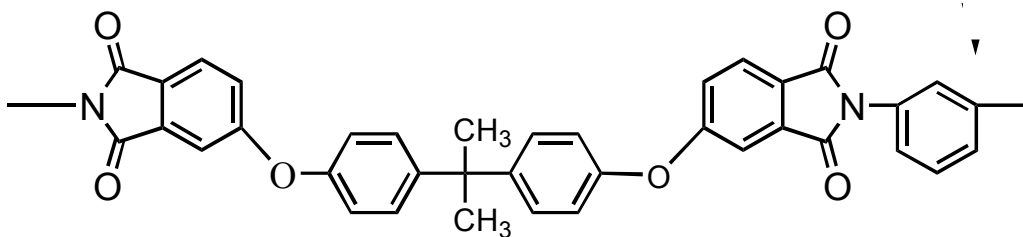

Figure 3: Chemical Structure Chain For Ultem[®] 1000

Ultem[®] is also known to have high heat resistance and structural stability up to its glass transition temperature of 217 degrees Celsius when cast and about 240 degrees Celsius when commercially produced.[6] Also, it can to be processed in a variety of ways, giving the polymer the flexibility to be used in variable fields.[7]

E. Nanoparticles

According to a recent IEEE paper by Roy et al., "Nanoparticle-filled polymers provide advantages because they provide resistance to degradation, and improvement in thermomechanical properties without causing a reduction in dielectric strength."[8] It further says that the several factors which could lead to this are the "'large interaction zone' or region of altered polymer behavior, changes in polymer morphology due to the surfaces of particles, a reduction of internal field caused by the decrease in size of the particles, changes in the space charge distribution, and a scattering mechanism."[9]

The addition of nanoparticles with higher ionization potentials to a polymer is thought specifically to increase the dielectric strength by preventing "treeing" or the spreading of ionized electrons. These more stable particles within the polymer prevent bond scission due to cascading electrons. Also, since electron affinity and ionization potential are proportional, these nanoparticles should be able to absorb avalanching electrons, further preventing breakdown.

Understanding the specific effects of each of these nanoparticles mechanisms is a goal of this study, and to observe these effects, samples of particle-filled polymers were made. Prof. Lomax of the United States Naval Academy Chemistry Department synthesized the SBA-15 Mesoporous Silica as shown in Figure 4. "Meso" means that the silica is between the nano and micro sizes, and "porous" means that the silica has a spherical hole in the center, which is a benefit in that it increases the surface area of the particle.

The silica was manufactured by combining TEOS (tetraethyl orthosilicate) and Pluronic 123™ (P123™) a non-ionic surficant made by Badische Anilin- & Soda-Fabrik (BASF). Under extreme temperature, the organic parts of these compounds burned off, resulting in a hollow molecular shell of silica with uniform diameter of approximately 10 nanometers. Surface pores

penetrate the shell allowing access to both the inner and outer surfaces of the nanoparticle. This results in a very large effective surface area. The silicas are characterized by the ratio of the template material P123™ to the silicon as an R value. The two R values provided were 45 and 75.
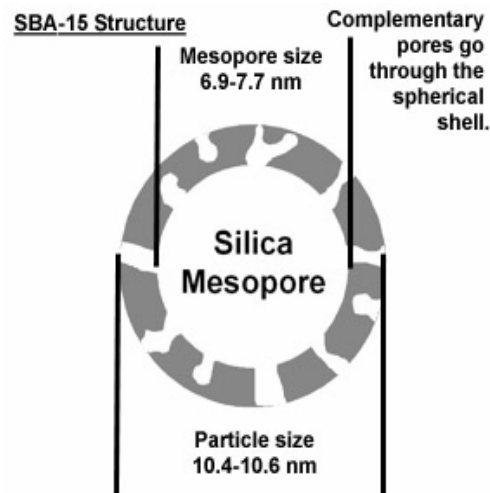

Figure 4: SBA-15 Structure

In addition to providing the base mesoporous silica, Prof. Lomax provided silica with polystyrene bonded to the surface. Polystyrene has been proposed as a way to increase compatibility with the Ultem® as well as assist in the improvement of breakdown strength. This proposed improvement is due to polystyrene's large size (0.6-20 micrometers) and electrical stability compared to polymers such as Ultem®. However, they have to be well dispersed, or their large size creates more free volume.

III. Materials and Instruments

The materials used in this study are listed below.

Polypropylene – thicknesses 7.8 and 9.8 micrometers, used as a control material for the initial breakdown measurements, manufactured by the Steinerfilm Inc.

Mylar[®] – thickness 5 mil (one thousandth of an inch), used as another control for initial breakdown testing

Ultem[®] - GE polymer, 1 mil Ultem 3000, 2 mil Ultem 1000, and 5 mil Ultem 5000, provided by Dr. Clive Reed

Solution Cast Ultem – cast polymer of varying thickness, studied in pure state and with the addition of mesoporous silica of varying proportions

SBA-15 Mesoporous Silica - mesoporous silica to be added to the cast Ultem[®]

1-Methyl-2-pyrrolidinone – solvent used in preparation of Ultem[®] cast films

Fluorinert[®] - electronic liquid FC[®]-77 made by 3M used as an insulator to the environment in the dielectric strength testing process

The instruments used in this study included two sample preparation apparatus', two breakdown testers, two set-ups for the testing of dielectric constant and loss over a range of temperatures, and a X-ray powder diffractometer to test for the crystallinity of the samples.

Denton Vacuum Desk II Turbo Sputter Coater

Hipotronics AC/DC Hipot Test Set

Quadtech Guardian 20kV DC Hipot Tester

Phillips X-ray Diffractometer

Thermolyne Type 6000 Programmable Ashling Furnace

Denton Vacuum Evaporator

Andeen 10Hz-100kHz Capacitance Bridge Model CGA-83

Lakeshore Cryogenics DRC 82C Temperature Controller

Novocontrol Technologies Quatro Cryosystem

2x HP 6038A System Power Supplies

Cryogenic Associates Cryogenic Chamber

MATLAB™ software

Microsoft EXCEL™ software

IV. Methods

A. Dielectric Breakdown Measurements

In order to test dielectric breakdown, the sample must be prepared. The films of commercially produced material being tested were cut into squares approximately two and a half inches on each side. The films were sputter coated with gold using the Denton Vacuum Desk II Turbo Sputter Coater. One side was coated completely and was used as a ground during the testing. The other side was covered with a mask shown Figure 5. Each sample square had sixteen electrodes so that a number of tests could be performed on each sample. The statistical nature of breakdown requires numerous trials to evaluate the behavior and will be discussed in a later section.
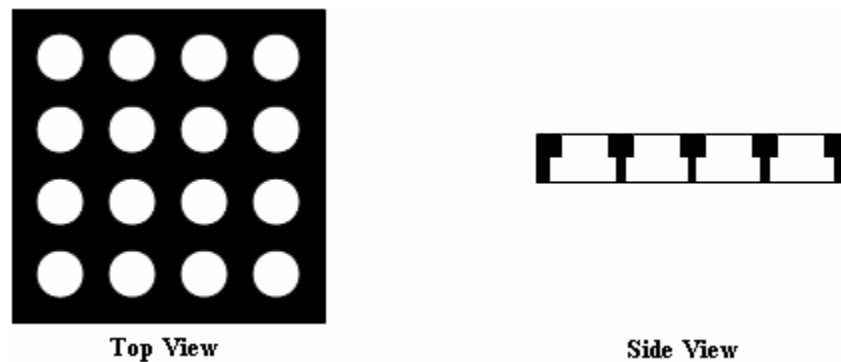

Figure 5: Dielectric Strength Sputtering Mask

The holes in the mask were raised so that the gold contacts would taper in thickness as they reached the edge of the circle. This was to prevent edge breakdown. Edge breakdown is not desired, because it does not reflect the proper breakdown strength of the material but a breakdown due to electrode shape instead. The Denton Vacuum sputter current was run for sixty

seconds at fifty percent power for all shapes in order to maintain consistent thicknesses of the electrodes, which were on the order of 0.2-0.3 micrometers.

The sample was then placed in a holder which had a stainless steel base to create contact with a grounding side of the film sheet. A plastic block with sixteen holes matching the electrode geometry was placed on top. The rig was then placed in a Petri dish, and the dish was filled with Fluorinert® in order to prevent surface arcing from prematurely ending the test. Testing of the sample was done using either the Hipotronics AC/DC Hipot Test Set or the Quadtech Guardian 20kV DC Hipot Tester. For each test a 1 centimeter diameter rod attached to the voltage output of the machine was lowered through the hole onto the circular electrode and a measurement was taken. For each measurement the voltage applied to the sample was increased at a rate of 500 V/s until a current of 1mA was measured by the tester. At this amperage it was assumed the capacitor had become a conductor and thus breakdown had occurred. The rod was then lifted and placed on to another test point until all sixteen were used on a sample. The sample rod was cleaned after every 4 tests.

In order to test Ultem® samples with mesoporous silica they had to be cast from a solution. First an established mass of mesoporous silica was weighed and dissolved in the solvent 1-Methyl-2-pyrrolidinone. This solution was then place in an ultrasonicator for approximately an hour to attempt to break up any agglomeration of the silica. Then, the proportional mass of commercially available Ultem® beads was added to obtain the mass percentage of solution desired. This solution was placed on a hot plate with a magnetic stirrer and heated to approximately 120°C in order to mix the solution and evaporate excess solvent. Once the solution reached a thick consistency, it was poured onto a sheet of steel shim stock and spread with a doctor blade in order to achieve a desired thickness. The remainder of the solvent

was then evaporated off the sample by heat treating it in the oven for one hour at 150°C for initial evaporation and then one hour at 220°C. The sample was allowed to cool, and a 2.5 inch by 2.5 inch section was cut to include the steel shim stock backing. Finally, the 16 testing point mask was used to gold sputter electrodes onto the sample, and the sample was tested as before, with the only difference being the steel shim stock was used to ground the sample as opposed to a gold sputtered electrode.[10]

B. Broadband Dielectric Spectroscopy Measurements

Dielectric spectroscopy of the materials was performed to determine the dielectric constant and loss. These measurements were done using a set-up created by Professor Fontanella of the United States Naval Academy Physics Department. One inch square samples were coated with aluminum as shown in Figure 6.

Bottom Side   **Top Side**

Figure 6: Broadband Dielectric Spectroscopy Sample Mask

Careful preparation of the electrodes is required to create a consistent electric field. This is due to the fact that when an electric field reaches a sharp edge it fringes, or bends out. This weakens the field and creates data which does not reflect the true behavior of the dielectric being tested. This sample preparation allows for the measurement of the center ring to be done with straight field lines, and the outer "guard" ring to supress the fringing field lines. An additional benefit is that the guard ring is able to shield the center ring from outside capacitances, allowing the collection

of even more accurate data. Figure 7 shows a side view of this sample preparation with simulated

electric field lines to illustrate the fringing protection of the guard ring.

Figure 7: Electric field lines on a sample with guard ring

Once the samples are prepared, up to eight were placed into a sample holder specifically

designed to place the same electric field upon the center and guard rings and also to take data

upon the center ring. There were two test rigs for these experiments, one for lower temperatures

ranging from 6 Kelvin to 350 Kelvin using the Cryogenic Associates Cryogenic Chamber and

one for higher temperatures ranging from 130 Kelvin to 670 Kelvin using the Novocontrol

system.

The sample was then placed in either of the sample cells of the Novocontrol or Cyrogenic

Associates system. For the Cryogenic Associates system, the chamber was then cooled using

both liquid nitrogen and eventually liquid helium at staged increments controlled by the

Lakeshore Cryogenics DRC 82C Temperature Controller to approximately 6 Kelvin. For the

Novocontrol system, nitrogen gas from a heated liquid nitrogen dewar was used to raise and

hold the sample at the desired temperatures. During each stage, an AC signal at 17 equal

logarithmic intervals from 10 to 100000 Hz was applied to each sample, and measurements of

the resulting capacitance and conductance were measured using the Andeen Capacitance Bridge

Model CGA-83. The capacitance (C) and conductance over frequency ($\frac{G}{\omega}$) were output to a

computer.

The geometric constant was calculated by using the measurement at room temperature and at 1000 Hz as a reference. Using the equation relating capacitance to dielectric constant ($C = \dfrac{\varepsilon' \varepsilon_0 A}{d}$), we are able to calculate the ε', or dielectric constant, for the first measurement. Then, by taking this and dividing by the capacitance we get the geometric constant. This is then used to manipulate all other data since we can assume that:

$$\varepsilon'_{any} = \varepsilon'_{RoomT} \left(\frac{C_{any}}{C_{RoomT}}\right) \qquad\qquad \text{Eq. 17}$$

Therefore, by multiplying the geometric constant times the capacitance from the measurements we have the dielectric constant for that measurements temperature and frequency.

In order to determine dielectric loss, the conductance over frequency ($\dfrac{G}{\omega}$) must be used. To do this, our definition for conductance is utilized, where ε'' is the dielectric loss. However, dielectric loss is commonly presented as:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{G}{\omega C} \qquad\qquad \text{Eq. 18}$$

So, to obtain this $\tan \delta$ we simply divide the conductance over frequency by the capacitance for that measurement.

C. X-ray Diffraction

In initial samples, the cast Ultem® film containing mesoporous silica was found to be brittle. X-ray diffraction was used to test for the possible onset of crystallization which might contribute to the brittle nature of the film. The cast sample and glass substrate was cut and placed into the Philips X-ray Diffractometer. The diffractometer uses the Copper K$_\alpha$ wavelength. The diffracted beam intensity was measured for a range of 2θ angles from 10 to 45 degrees. The intensity measured in counts was exported to the program X'pert Industry™, which was used to

graph the counts as a function of 2θ. An example of the X-ray diffraction plot for Ultem[®]

containing 2% R45 with polystrene coating (PS) is shown below. No crystallinity was detected

by this method. Control scans of the bare glass substrate show the peak at 36° to be due to the

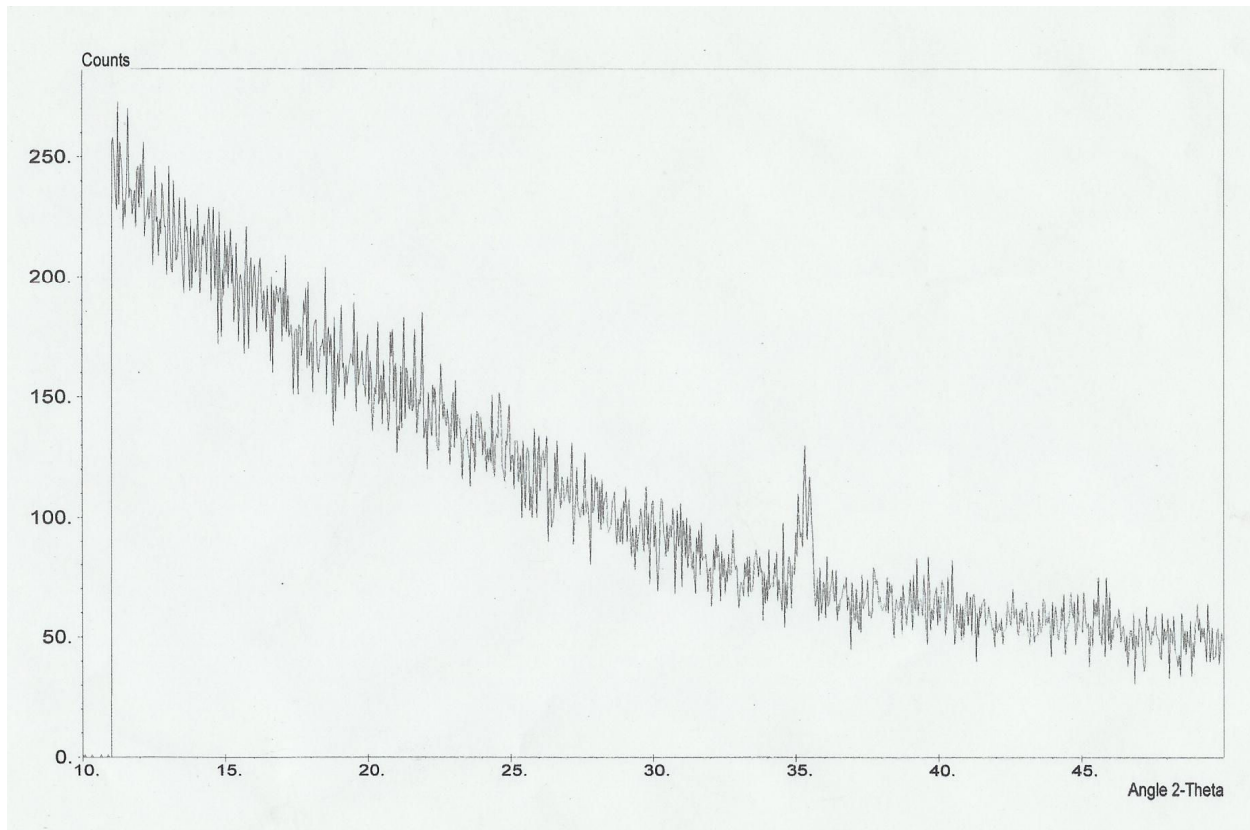substrate, and are not Ultem[®] related.

Figure 8: X-ray Diffraction of Ultem[®] 2% R45 PS

V. Results

A. Dielectric Breakdown Measurements:

The initial breakdown measurements were conducted on 7.8 and 9.8 micrometer thick

polypropylene, a dielectric material with widely published data. This was to ensure the accuracy

of our test setup and to adjust the rig so that consistent results could be achieved. Original testing

was done using aluminum electrodes. Thermal damage of the polymer that occurred during the

aluminum vapor deposition forced us to change the electrode material and coating process. This damage was avoided by switching to gold sputtered electrodes. Also, gold sputtering took about one half as long to prepare a sample. Once the electrodes were applied, the sample was transferred to the test rig. A ramping test voltage was applied to one set of electrodes until breakdown was observed. This was repeated a number of times on the same electrodes for both the polypropylene and Mylar™ in order to see the effect of the "self-healing" mechanism reported in polypropylene.
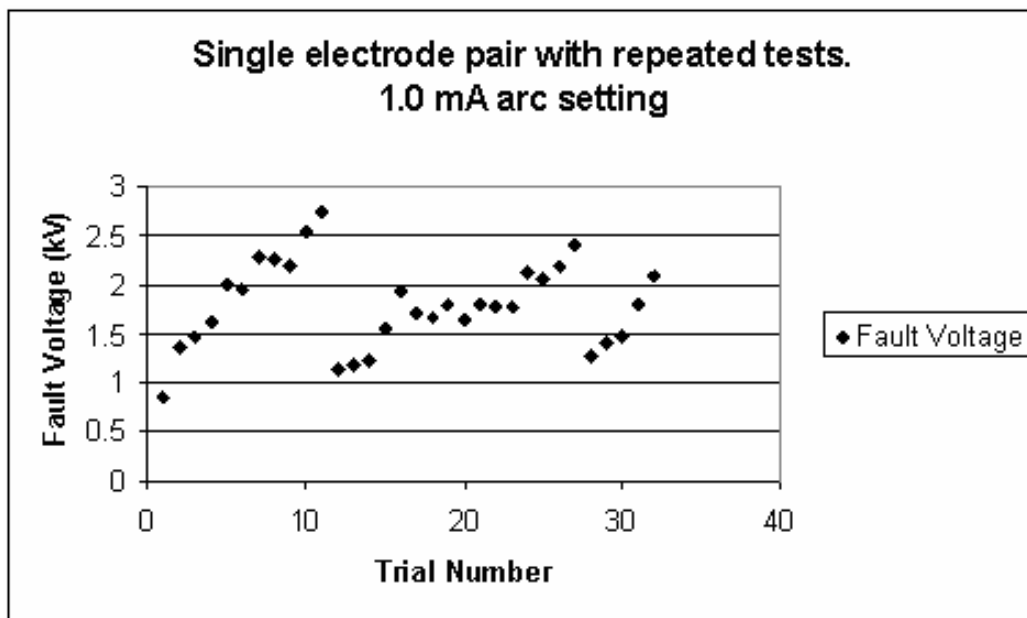

Figure 9: Repeated breakdown testing on a polypropylene sample

"Self-healing" is a term used to describe the ability to re-use a sample after breakdown occurs. When a breakdown occurs it may result in evaporating the electrode area around the defect, preventing an electrical short at the breakdown site. The outcome is it is possible to reuse a material even after dielectric breakdown has occurred. Not all materials exhibit self-healing, and so it is a desirable trait amongst dielectrics. Also, manufacturers take advantage of this trait by pre-treating capacitors, breaking them down several times, purging the dielectric of low

strength defects. This allows for a higher operating voltage and energy density. Evidence of self-healing was found during these tests as shown in Figure 9.

Next, a single measurement cycle was applied to a large number of polypropylene samples. These measurements were combined onto a single graph which used the cumulative probability of failure function to weight them. This is due to the stochastic nature of breakdown testing. Since breakdown is primarily due to defects in the material which are believed to be randomly distributed throughout the material, the results of breakdown measurements are variable in nature. Thus, in order to analyze the results, a probability distribution must be used with the median value used as the accepted value. Probability statistics have been used in other breakdown studies, normally through a Weibull distribution, further described in Appendix A, given as:

$$P_F(E_b) = 1 - e^{-\left(\frac{E_b}{a}\right)^b}$$ Eq. 19

where $P_F(E_b)$ is cumulative probability of failure (CDF). Throughout the project was the "mean rank approximation" was used to approximate the CDF and is defined as:

$$F(i,n) = \frac{i - .3}{n + .4}$$ Eq. 20

In this approximation i is the test number once all the recorded breakdown values are sorted from least to great for a given sample. n is the total number of tests taken on a single sample. This function has been proven to be a good approximation for the electrical breakdown tests[11] and the fifty percent probability of failure value was used to describe trends in the dielectric strength of the materials tested.
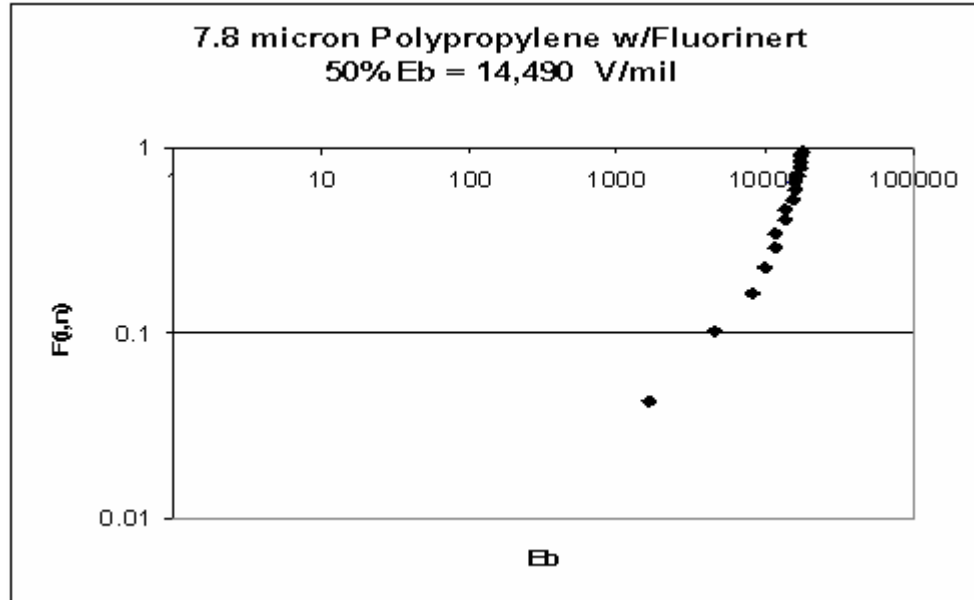
Figure 10: Polypropylene Breakdown Testing

Figure 10 shows the results for the 7.8 micrometer polypropylene tested. The relatively linear results from each sample suggest that a single mechanism is causing the breakdown of the dielectric. The failures also occur over a broad spectrum of voltages, believed to be to due the randomness of the defects within the material which cause the breakdowns to occur. Further, the two graphs show how an increase of thickness increases the voltage at which the breakdown occurs, validating the necessity of defining breakdown voltages as a measure of voltage per thickness. Finally, the bottom portion of the graphs show some rogue data points leading to a break in the slope which are believed to be due to faults in procedure or unnatural defects in the material such as surface defects caused by scratching or abrasion which maybe have weakened the material surface bonds. After several data runs on polypropylene we determined the value of 14,490 V/mil was consistent with the accepted dielectric strengths.

Ultem® was the next material studied. Solution cast Ultem® was tested for its dielectric strength. However, due to the casting process, not all of the cast Ultem® samples were of equal thickness. This led to a distribution of breakdown values, as shown in Figure 11.
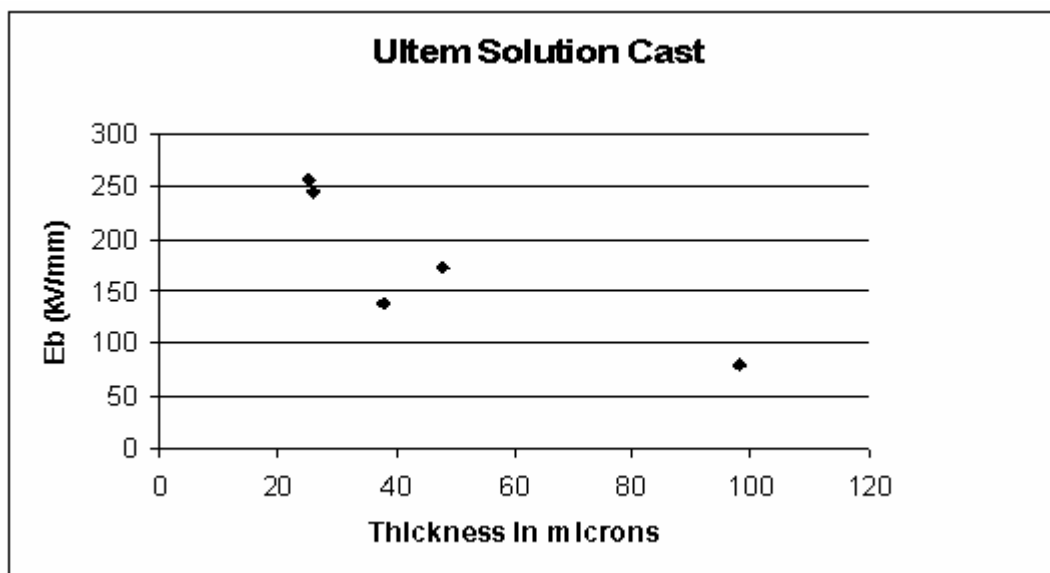

Figure 11: Solution Cast Ultem® Breakdown Strength as a Function of Thickness

This variation in the breakdown strength emphasizes two characteristics of the material. First, the thicker the material, the lower the breakdown voltage. This is supported by the theory of defects being the primary cause of breakdown in dielectric. A thicker sample has an increased volume, and thus increased probability of defects occurring within a thicker sample. This increase in defects gives rise to breakdown at a lower applied field

Second, the way in which the sample is cast has an effect on the dielectric properties. Surface defects as much as volume defects will have an effect on the breakdown strength of a sample. This is shown by the data point for approximately 38 micron thickness, which was noted to be exceptionally non-uniform in thickness.

In order to attempt to increase the dielectric strength, as Figure 11 shows, the cast samples were made as thin as possible. The thickness of 1-2 mil (thousandths of an inch) was the goal. However, since the cast samples were not all of the same thickness, and noticing the large effect this has upon the breakdown strength of Ultem®, the data was divided into groups depending upon the thickness of the sample, before being fit to a Weibull curve.
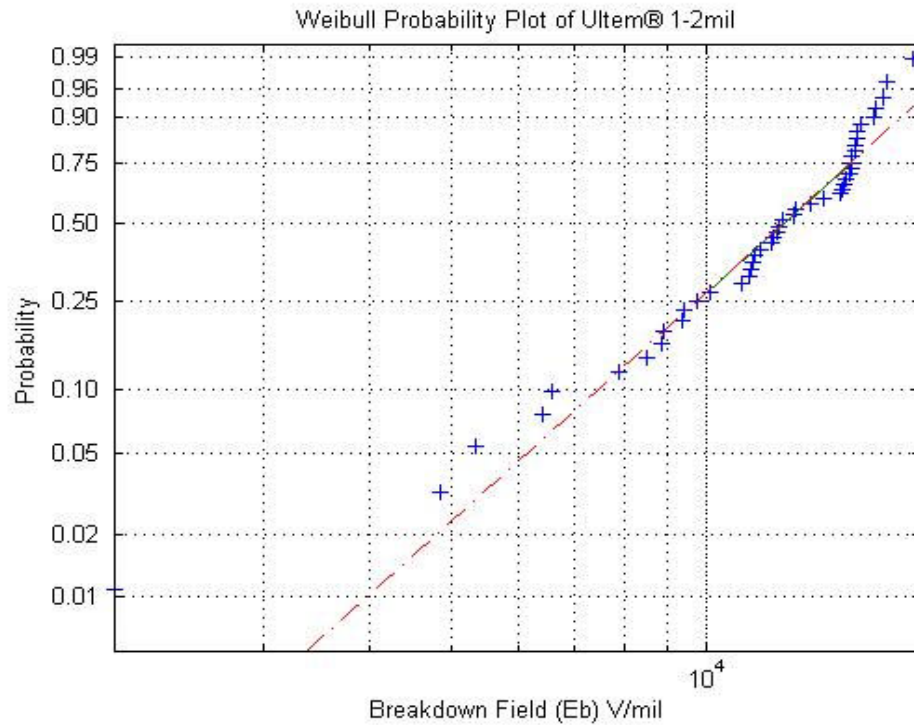

Figure 12: Weibull Probability Plot of Ultem® 1-2mil

Figure 12 shows the breakdown field values of solution cast Ultem® samples of thickness 1-2 mil on a Weibull plot. The dashed line shows the Weibull curve which best fits the set of data. The plot is on a logarithmic scale showing the exponential nature of statistical breakdown. The vertical axis of the graph displays the probability of a breakdown occurring at or below corresponding value. For this particular set of data the curve was fit using MATLAB™, which determined the Weibull coefficients for the cumulative probability of failure function Eq. 19 to a

scale parameter of $a = 13240$ with a 95% confidence interval of [12340, 14210] and the shape

parameter $b = 4.266$ with a 95% confidence interval of [3.342, 5.445]. Using this distribution it

was derived that the 50% value, or the median value of the function, was 12150 V/mil. A

comparative analysis of the 50% values for several thickness and filled percentages of Ultem® is

discussed in a later section.

B. Dielectric Spectroscopy

Originally, three samples of solution cast Ultem® and a sample of commercially produced

Ultem® 1000 were measured using dielectric spectroscopy. This was done in order to

characterize the dielectric properties of pure Ultem® samples. First, low temperature data were

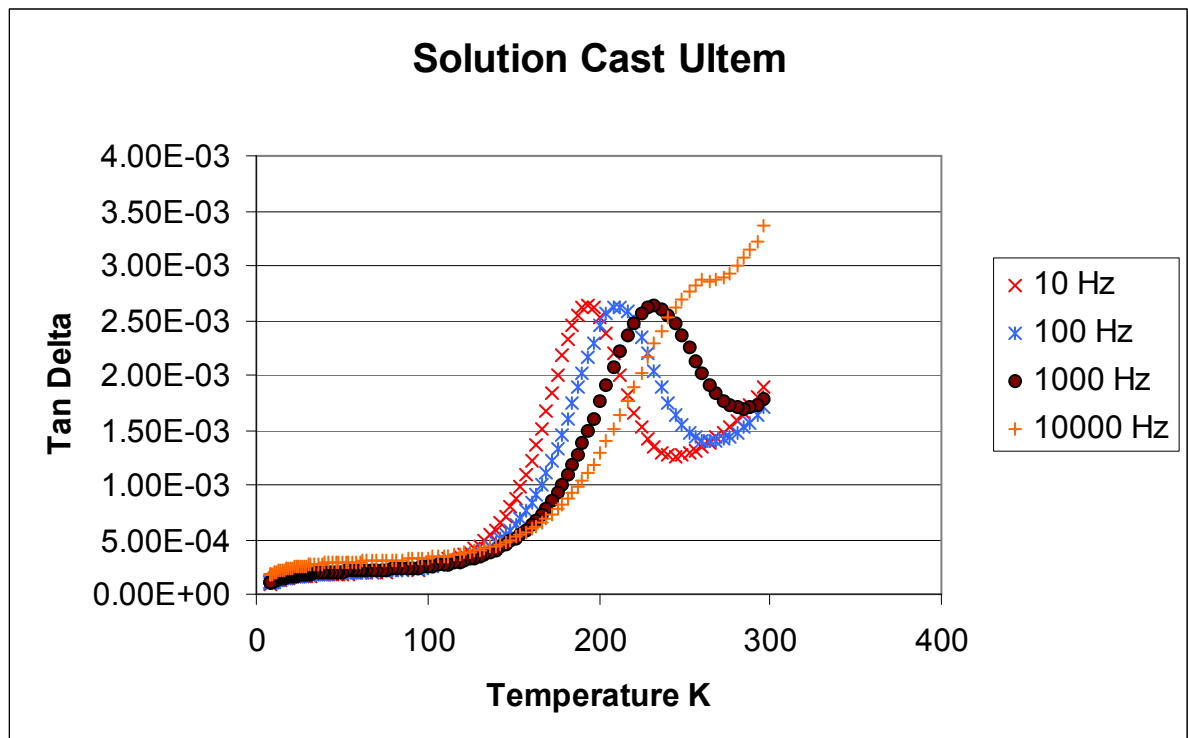taken. The observed $\tan \delta$, a measure of the dielectric loss, is shown in Figure 13 and Figure 14.

Figure 13: Solution Cast Ultem® Tan(δ)

Figure 13 shows the loss peaks for the solution cast Ultem®. These peaks are the result of the relaxation of the Ultem® towards conductivity at each frequency. This can be compared to the Ultem® 1000 where the water has been driven off by heating the material. These results are shown in Figure 14, and no loss peaks are prevalent at the same range as the "wet" solution cast Ultem® samples. This water dependence in the Ultem® has been previously noted.[12]
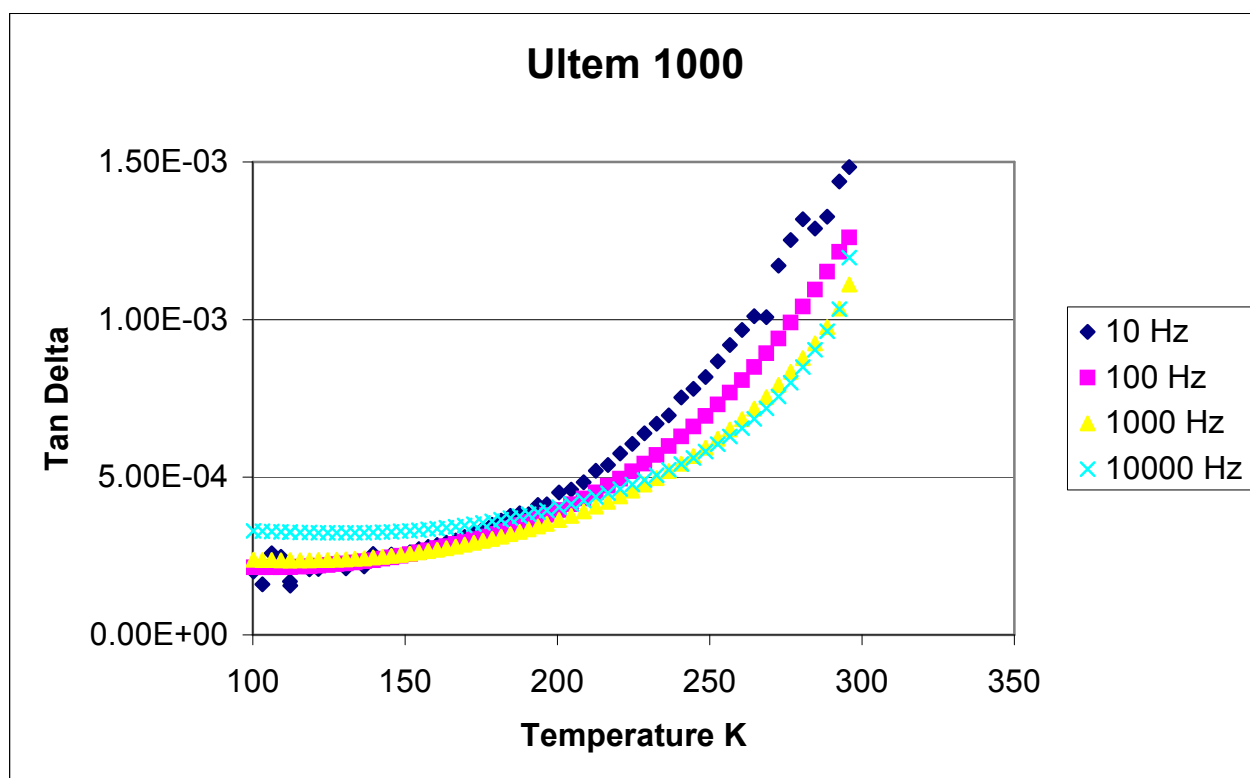

Figure 14: Commercially Produced Ultem® Tan(δ)

Figure 15 and Figure 16 show the dielectric constant of the same two samples as a logarithmic function of the applied AC frequency. These graphs show the trend in that the higher temperatures ε' drops with an increase in frequency and at lower temperatures it remains relatively constant, i.e. it exhibits very little dispersion. Thus at lower temperatures the time constant for the alignment of the dipoles is significantly less than the period of the applied

voltage over the frequency range of the test. At higher temperatures the time constant for the alignment of at least some of the diploes is similar to the period of the applied voltage. At lower frequencies a more complete alignment takes place and a higher dielectric constant is observed. The most significant observation for Figure 15 and Figure 16 is that the variation in the dielectric constant is small. From 7.58K to 264K and from 10Hz to 100kHz the variation in ε' for Ultem[®] 1000 was less that 1% and for solution cast Ultem[®] less than 2%
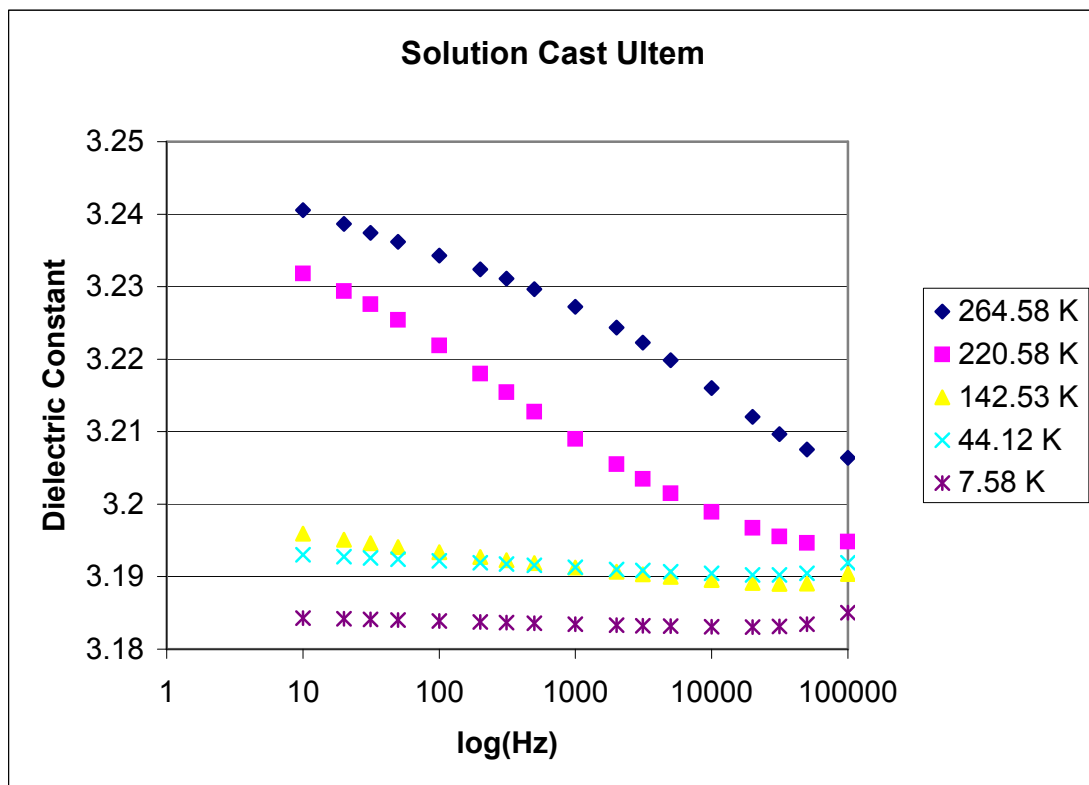

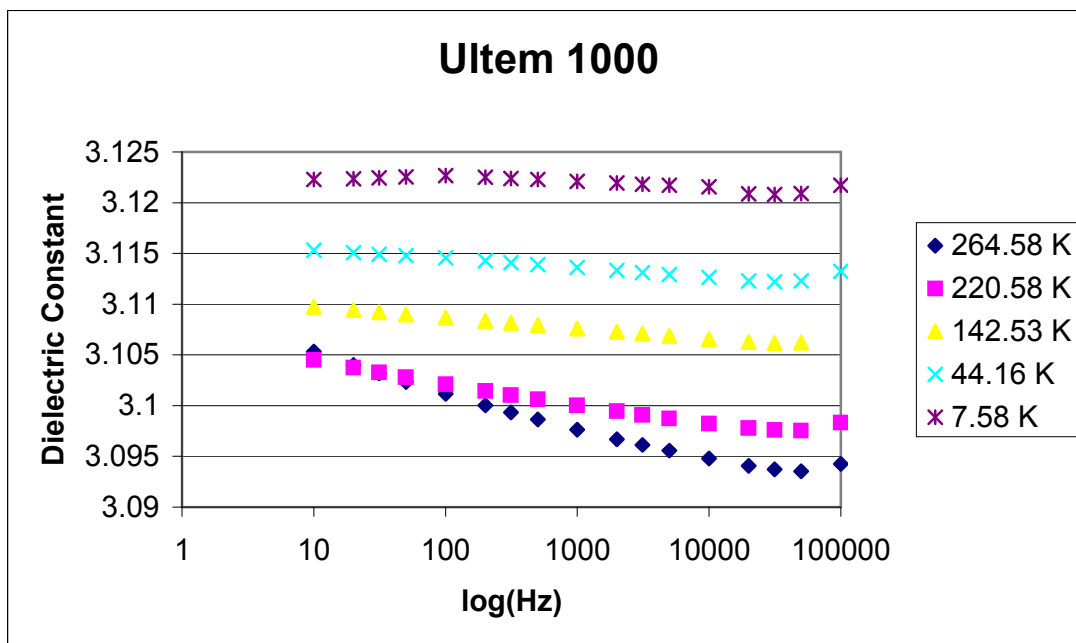**Figure 15: Dielectric Constant of Solution Cast Ultem[®]**

Figure 16: Commercially Produced Ultem® Dielectric Constant

After taking the low temperature data, and getting the Novocontrol rig set up since it arrived during the middle of the project, high temperature data of solution cast and commercially prepared Ultem® were taken. Both of these materials exhibited interesting behavior associated with the glass transition temperature. Figure 17 shows the effect of high temperature and frequency upon a pure Ultem® sample. This shows that Ultem® displays "classical" dielectric relaxation; that is the loss peak shifts to high temperatures and lower amplitudes, and the applied frequency is increased. This allows us to characterize the polymer and identify any characteristics the addition of mesoporous silica may induce upon Ultem®.
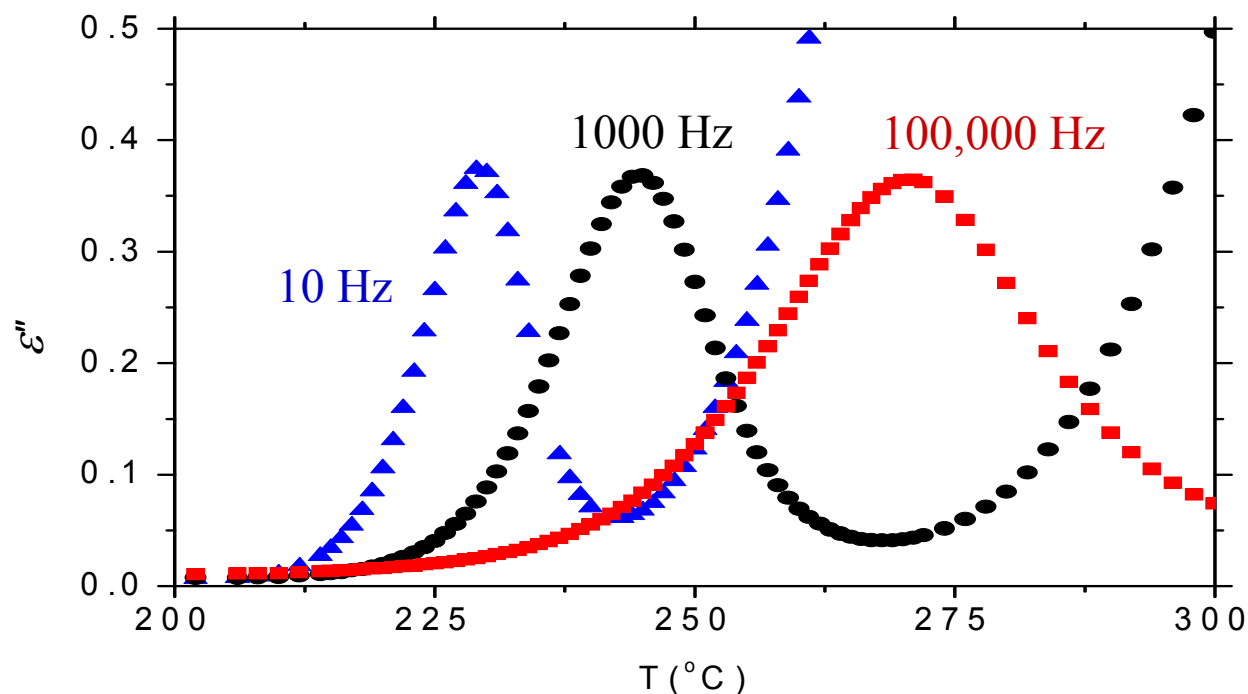
Figure 17: High Temperature Ultem® Loss Curves

C. Nano-particles

Mesoporous silica was added to the Ultem® polymer during the casting process. Early attempts at adding silica to the dissolved Ultem® did not result in an acceptable film. The first attempt was at a 5% weight percentage (wt-%) of SBA-15 R=75 mesoporous silica. This resulted in agglomeration of the particles in the film and thus an unusable sample. The next two attempts were at 2% and 0.5% wt-% of the same silica. These films were extremely brittle, cracking easily, and were tightly bound to the glass substrate.

A portion of 2% mesoporous silica Ultem® film underwent X-ray diffraction to see if the silica had created any crystallinity within the sample. The diffractometry in Figure 8 showed a crystal peak at angle 2θ of 36°. However, this same peak was observed when the glass substrate was tested without the film.

After these initial unsuccessful attempts an ultrasonicator was used to attempt to break up the agglomeration of the mesoporous silica. Using this instrument, combined with smaller percentages of nanoparticles, acceptable samples were made. Also, stainless steel was used as a substrate instead of glass. These samples were tested in a similar way to that used for the pure Ultem® samples. The resulting median values for the dielectric strength fields are shown in Figure 18.
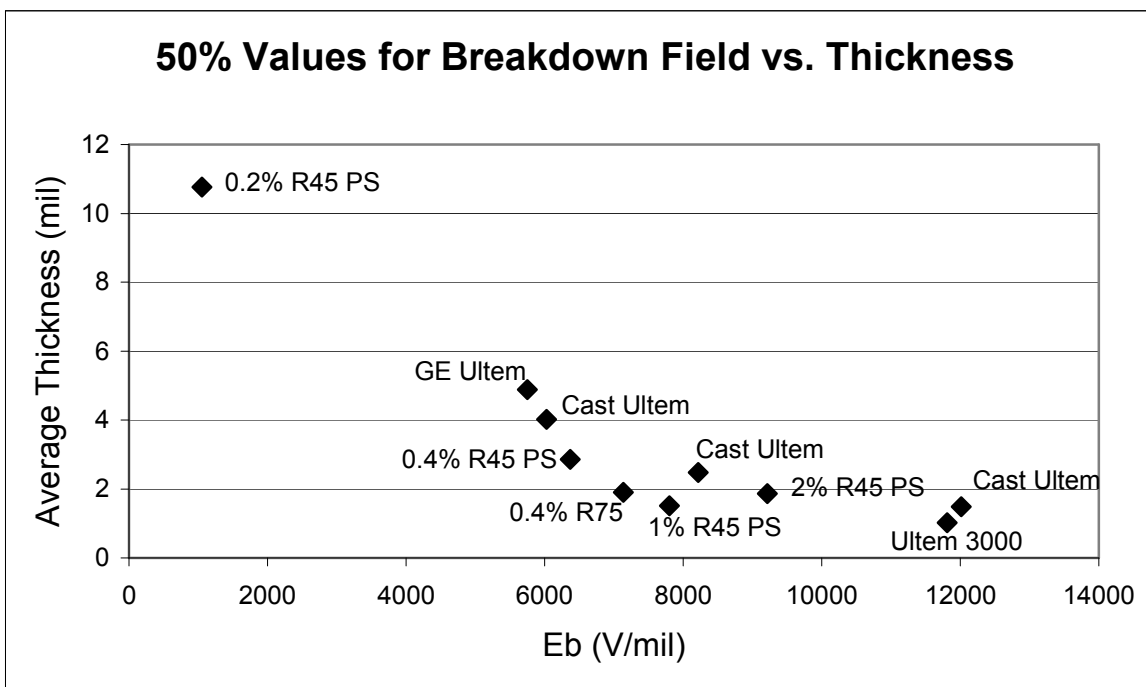

Figure 18: Combined Dielectric Data

From this graph of the median dielectric strengths for several types of pure Ultem® and mesoporous silica filled Ultem®, several things are evident. First, the process by which the material is made has a large effect on the dielectric strength. This is shown by the variation between solution cast Ultem® 1000 and commercially produced Ultem® 1000. Second, thickness again is a determining factor in the dielectric strength of the material. Finally, it was found that the addition of small percentages of mesoporous silica has a detrimental effect on the dielectric

strength of the material. However, the difference between the 1.5 mil 0.4% R45 polystyrene treated (PS) sample and the 1.0% R45 PS sample of the same thickness suggests positive results for the addition of that type of mesoporous silica in larger quantities. This variation could be due to the smaller percentage not having an even distribution throughout the material, creating more free volume. This additional free volume led to breakdown at lower potentials than the gains from the ability of nanoparticles to stop the cascade of electrons. Therefore a larger weight percentage of nanoparticles, being more evenly distributed, would have a greater ability to influence the dielectric properties of the host Ultem[®].

With respect to the dielectric spectroscopy, there were also important differences between the pure Ultem[®] samples and the nano-filled samples. At low temperatures the filled particles displayed a new loss peak which increased in magnitude and temperature as frequency was increased, as shown in Figure 19.
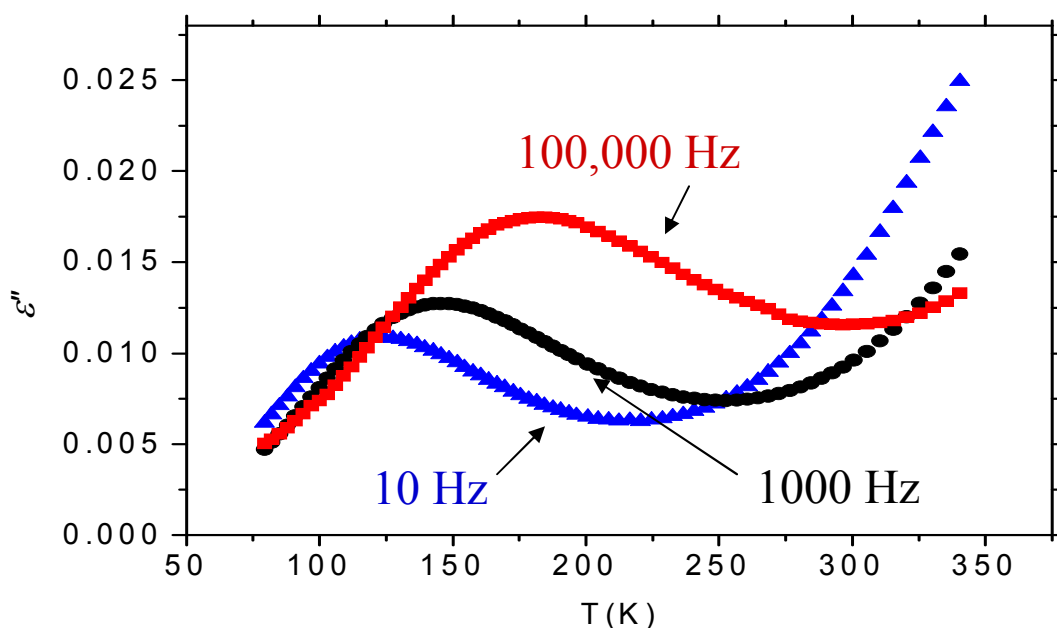

Figure 19: Low Temperature Filled Ultem[®] Loss Curve

This new loss peak is a point of concern in that it suggests the nanoparticles have an adverse effect upon the basic capacitor usage of the Ultem® to long term usage. Also, since the loss peak grows with frequency, any room temperature high frequency applications may not be feasible due to the large losses involved.

The preparation of the nanoparticles with respect to polystyrene treatment appears to have a large effect upon their influence of Ultem®. Figure 20 shows the low temperature reactions of commercially produced nanoparticle filled Ultem®, or "dry" Ultem® which had been shown to not have a water dependence, and "wet" filled solution cast Ultem®. These types of Ultem® were cast with two types of mesoporous silica, uncoated and coated with polystyrene. The effect of the polystyrene is a large loss peak across a wide range of temperatures. This leads to the assumption that the polystyrene makes the nanoparticles more incompatible with Ultem®. These losses, therefore, are probably due to the relaxation of the styrene units on the surface of the nanoparticles.
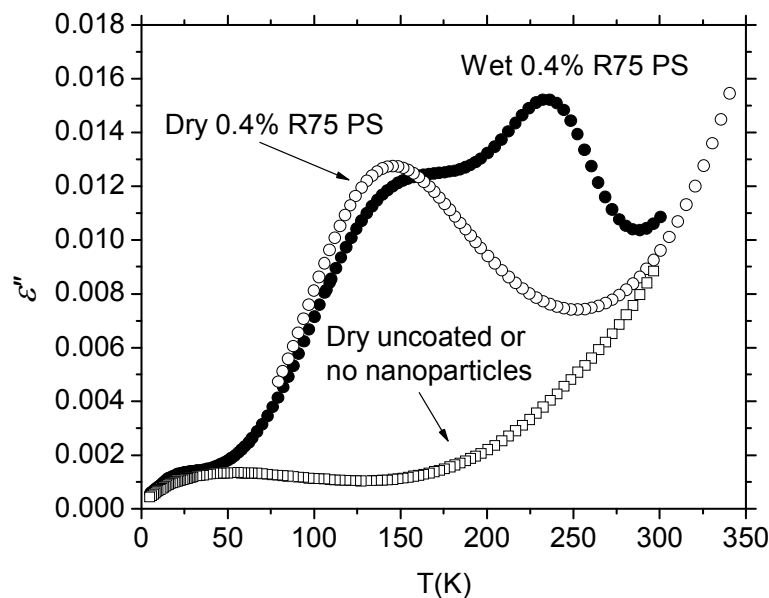

Figure 20: Low Temperature Filled Ultem Loss Curve With and Without Polystyrene

Figure 21 shows the loss measurements at high temperatures comparing a nanoparticles filled sample, a cast sample, and a commercially produced sample of Ultem®.
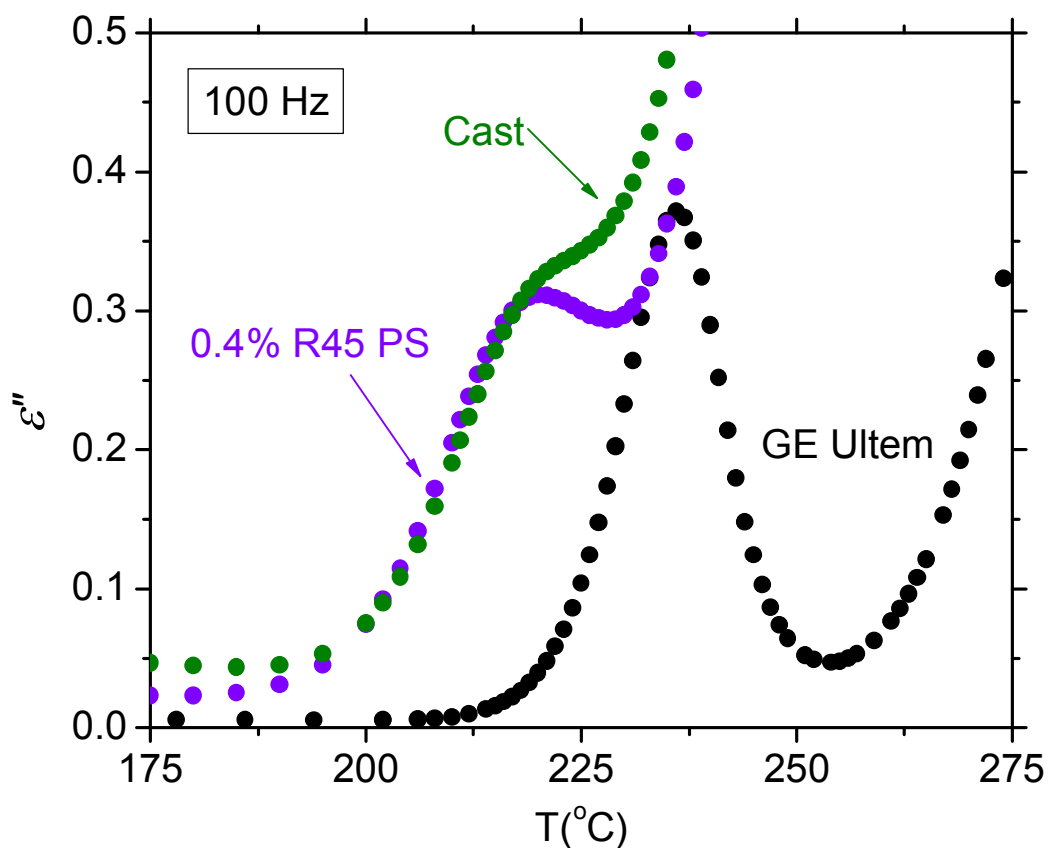

Figure 21: High Temperature Ultem® Loss Curves

The high temperature data shows a shifting of the glass transition peak of the samples. The difference in peak temperatures between the solution cast and filled samples is relatively minor, suggesting that the major reason for a shift in the peak is the casting process. However, the fact that there was no improvement or reduction in the peak magnitude or location suggests that either the filled particles are of insufficient concentration, since only up to 0.4% wt-% was

tested, or that they have absolutely no effect upon the glass transition temperature of the Ultem[®] samples.

VI. Conclusion

A new dielectric strength test setup was created, refined, and validated for use at the United States Naval Academy. This new rig allowed for scientific study of dielectric materials in a controlled environment, something not previously available at the Naval Academy. Validation of the test setup was done using polypropylene and Mylar[®]. Ultem[®] in both commercially produced and solution cast forms were tested defining the dielectric strength characteristic of the Ultem[®] polymer. A strong dependence on thickness was observed with the thinnest samples producing a dielectric strength of 12,010 V/mil and an energy density of 3.17 J/cc. This analysis of Ultem[®] had not been previously reported and shows that Ultem[®], when properly prepared, can reach the Navy's short term dielectric goal of 3-5 J/cc.

Mesoporous silica were added to the solution cast Ultem[®] with the hopes of improving the breakdown strength. The resulting data showed that a small addition of nanoparticles reduced the breakdown strength of the material. This is believed to be due to an uneven distribution of particles and the polystyrene surface treatment bonded to the nanoparticles. X-ray diffractometry was used to determine if any crystallization has occurred in the brittle samples, but no evidence supporting crystallization was found.

Dielectric spectroscopy measurements show that pure solution cast Ultem[®] is similar to commercially produced Ultem[®], especially with respect to a water loss peak observed between 220-230K at 1kHz, reaching a loss tangent on ε'' of 0.015. The addition of mesoporous silica coated with polystyrene created an additional loss peak at low temperatures, around 150K at 1kHz with a magnitude of ε'' of 0.013 and overlapping the low temperature water loss peak.

Neither of these peaks were noticed in "dry" Ultem® without nanoparticles. At high temperatures, especially around the glass transition temperature, the addition of nanoparticles had no effect upon Ultem's® dielectric loss, but the solution casting process did produce a small shift in the glass transition temperature from approximately 240°C to approximately 217-220°C.

Combined, these results show that Ultem® is a material with great potential as a dielectric. The addition of nanoparticles failed improve upon its dielectric properties, however, this is thought mainly to be due to incompatibility, yet this technique still holds promise for improveing the dielectric performance. Ultem® alone, is an exceptional polymer and should be considered when dielectrics that can withstand mechanical and thermal extremes are desired.

VII. Future Work

Future work should focus on how to increase the compatibility of nanoparticles with the Ultem® polymer. This includes replacing the polystyrene with the surface treatments that bond to the Ultem®. This should eliminate the polystyrene loss peak and perhaps improve crystallinity within the material. An increase in crystallinity could produce gains in the dielectric strength. Also, larger weight percentage of nanoparticles which are more evenly dispersed in Ultem® should be dielectric strength tested. This should allow for more bonding to offset the losses due to increased free volume.

Appendix A: Weibull Distribution

One of the main challenges with dielectric breakdown measurements is its stochastic nature. Stochastic measurements mean if the same measurement is taken on similar samples, a variety of results will be obtained. As such, statistical methods must be used in order to obtain information on the properties being tested. For failure testing, such as breakdown, lifetime distributions are used.[13] For this project, since lifetime distributions are impossible, the voltage was ramped at a 500 V/s. So by multiplying the time of failure by this ramp rate a breakdown voltage is given and a breakdown field E_b can be determined.

For failure testing multiple tests are taken on similar samples in order to obtain a data set of the desired property, in this case breakdown voltage. In this data set each sample is weighted equally and put into a histogram.
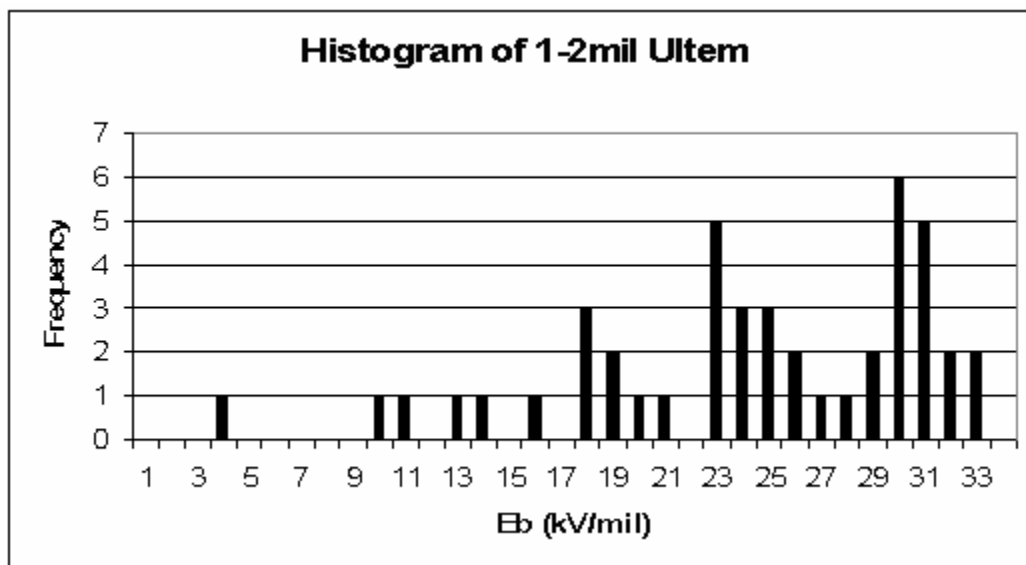

Figure 22: Histogram of Ultem® Breakdown

In this histogram, data points are divided into bins, or groupings, by the breakdown field observed. Each bin includes a range of 500 V/mil and there were 45 data points. From this histogram, a curve following the frequency for each breakdown field value can be drawn. This is

called a probability density function, normally designated as $g(E_b)$, which designates the probability of obtaining any one value if the test is repeated on a similar sample.

However, since the object of interest is not the frequency of a breakdown value but rather its probability of breaking down at a certain value, another histogram must be created.
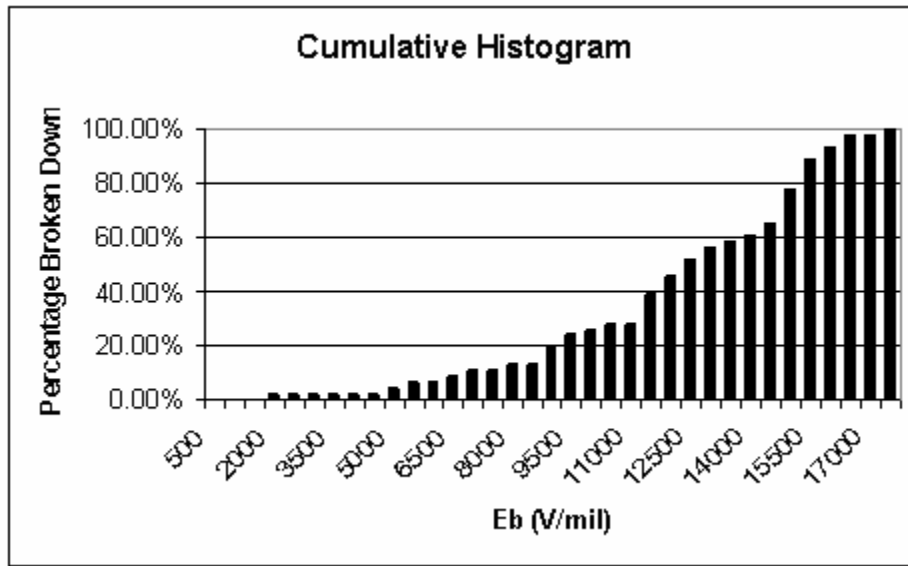

Figure 23: Cumulative Histogram of Ultem® Breakdown

The curve following the general outline of the peaks of this histogram is called the cumulative probability of failure, given by the function $P_F(E_b)$, where $P_F(E_b)$ is the probability of a given sample to breakdown at a time equal to or less than E_b. Since this is the format desired for values of breakdown, the cumulative probability of failure is the preferred format for breakdown analysis. The preferred form of this is the Weibull distribution.

Agreed on by the Institute of Electrical and Electronics Engineers, Inc. (IEEE) as the as an appropriate distribution for solid insulating systems, the Weibull distribution[14] allows for two degrees of freedom in the cumulative probability of failure distribution of $P_F(E_b) = 1 - e^{-\left(\frac{E_b}{a}\right)^b}$.

The parameters *a* and *b* are called the scale and shape parameters, respectively. Together, these allow a shaping of the Weibull distribution to fit provided data.[15] Examples of how each of these parameters affect the distribution is shown below.
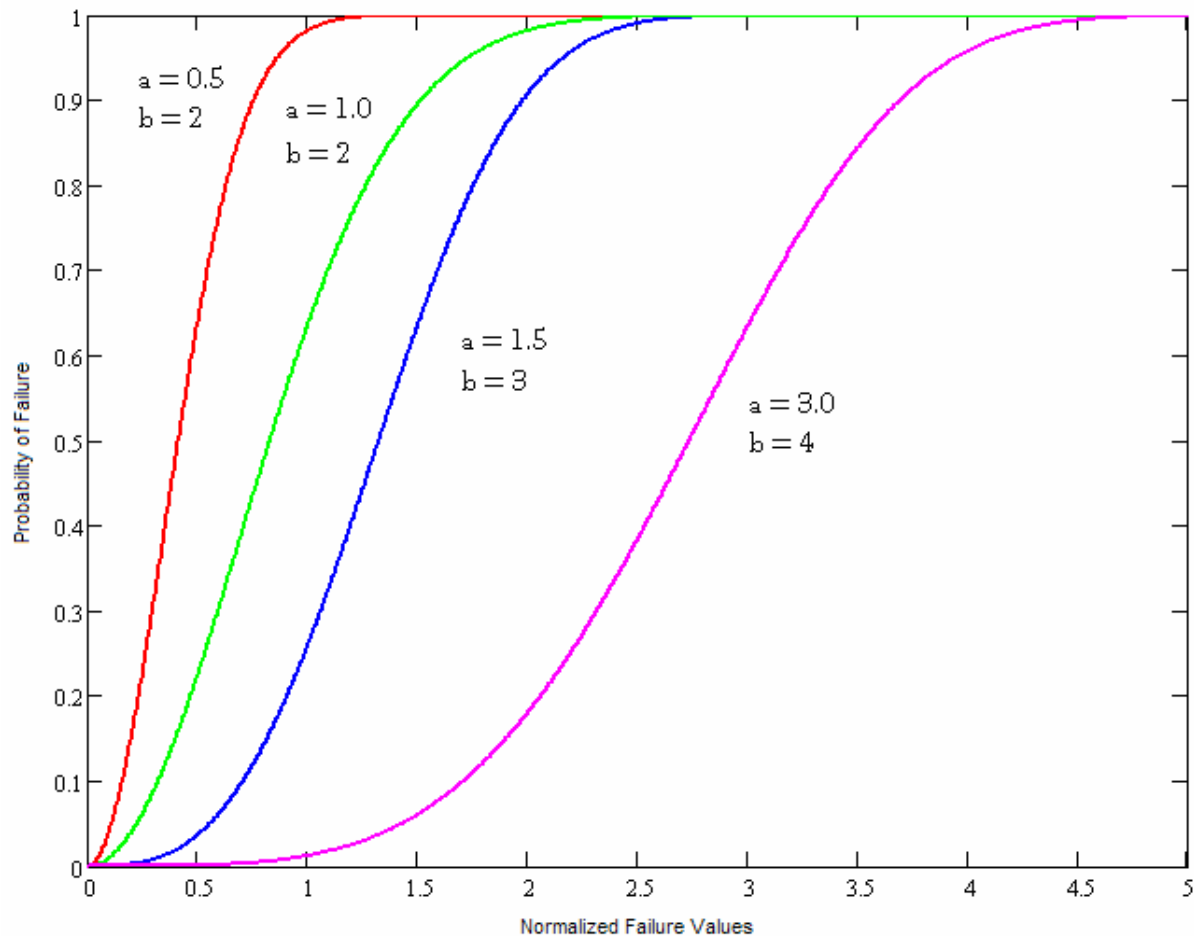

Figure 24: How Parameters Effect Weibull CDF[16]

The fitting of these Weibull parameters to a set of data is quite complicated and can be done by guesswork on a logarithmic graph or through normalizing the data. To aid in this process, MATLAB™ was used to fit the Weibull parameters for a given set of data points along with confidence intervals for each of these values. MATLAB™ also plotted Weibull curves, which are cumulative probability of failures on a logarithmic scale, so that the exponential decay

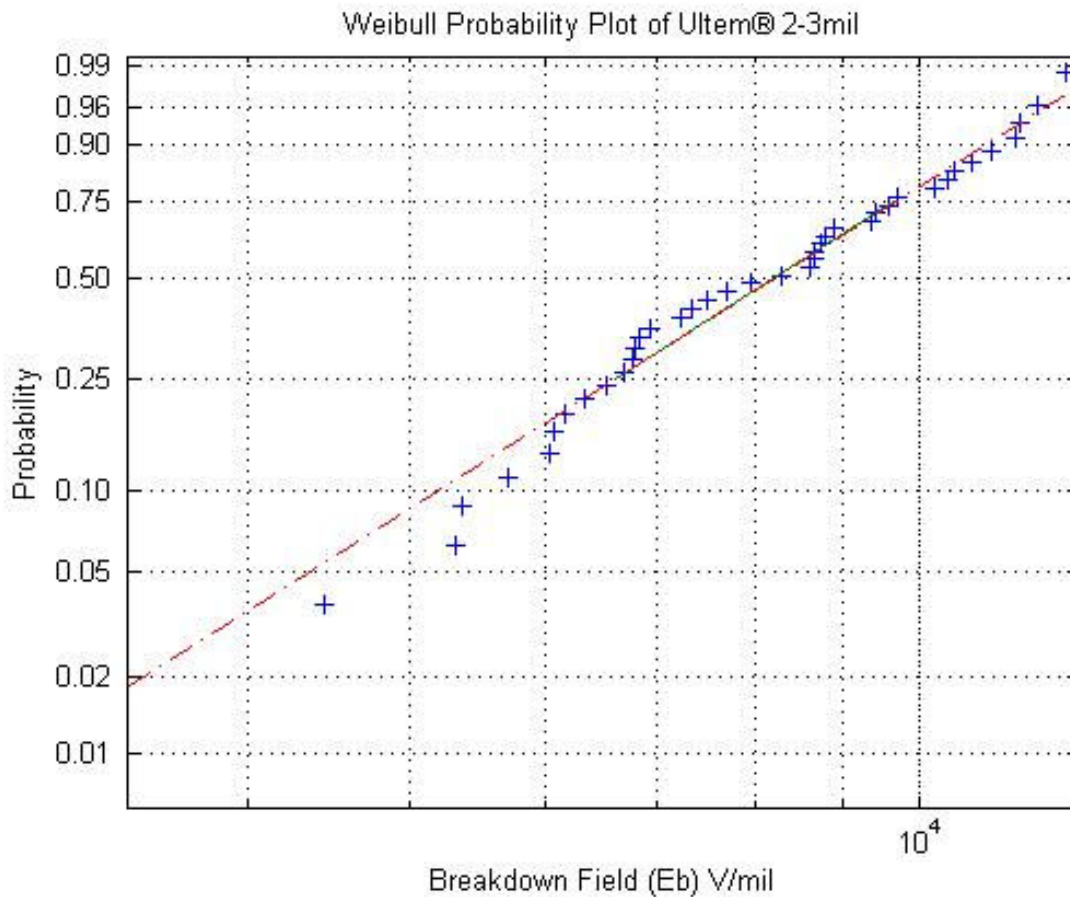of the distribution can be seen linearly. Examples of these graphs can be seen on page 30 and in Figure 25.

Figure 25: Weibull Cumulative Probability of Failure Plot of Ultem® 2-3 mil as a Function of Electric Field

---

[1] Costa, U. M. S.; Freire, V. N.; Malacarne, L. C.; Mendes, R. S.; Picoli, S., Jr.; de Vasconcelos, E. A.; da Silva, E. F., Jr. *An improved description of the dielectric breakdown in oxides based on a generalized Weibull distribution*. **2005**, 5.

[2] Irene, Eugene A. Electronic Materials Science. Wiley, Hoboken, New Jersey. **2005**.

[3] Cho, Y.; Park, J.; Shim, M.; Sang-Wook, K. *Effects of Defects on Dielectric Breakdown Phenomena and Life Time of Polymeric Insulation*. **1997**, 4, 447.

[4] Ohanion, Hans C.; Markert, John T. Physics for Engineers and Scientists 3rd Ed. W.W. Norton & Company, New York. **2007**.

[5] Fontanella, J.J.; McLin, M.G.; Wintersgill, M.C. *Journal of Polymer Science* **1994**, 32, 501.

[6] Theoleyre, S.; Reed, C.W. *Dielectric Properties of Polyetherimide Films*. **1984**, 5.

[7] GE™ Plastics. "Ultem® Resin."

      http://www.geplastics.com/gep/Plastics/en/ProductsAndServices/ProductLine/ultem.html

[8] Roy, M.; Nelson, J.K.; MacCrone, R.K.; Schadler, L.S.; Reed, C.W.; Keefe, R.; Zenger, W. *IEEE Transactions on Dielectrics and Electrical Insulation*. **August 2005**, 15, 629.

[9] Ibid.

[10] Theoleyre, S.; Reed, C.W. *Dielectric Properties of Polyetherimide Films*. **1984**, 5.

[11] Fothergill, J.C.. *IEEE Transaction on Electrical Insulation*, **June 1990**, 4, 489.

[12] Fontanella, J.J.; Bendler, J.T.; Schuele D.E.; Edmondson, C.A.; Lomax, J.F. *Effect of pressure on the water relaxation in Ultem® polyetherimide.* Accepted to *Journal of Non-Crystalline Structures* **Nov 11 2006**, 6.

[13] Dissado, L.A.; Fothergill, J.C. Electrical Degradation and Breakdown in Polymers. Peter Peregrinus Ltd., London. **1992.** 319-355.

[14] *Guide for the statistical analysis of voltage endurance data for electrical insulation.* ANSI/IEEE Std. 930-1987. **1987.**

[15] Weibull, W. *A statistical distribution function of wide applicability.* J. Appl. Mech.-Trans. ASME 18(3), 293-297. **1951.**

[16] Leitch, Philip. http://en.wikipedia.org/wiki/Image:Weibull_CDF_2.PNG

VII. Bibliography

Cho, Y.; Park, J.; Shim, M.; Sang-Wook, K. *Effects of Defects on Dielectric Breakdown Phenomena and Life Time of Polymeric Insulation*. **1997**, 4, 447.

Costa, U. M. S.; Freire, V. N.; Malacarne, L. C.; Mendes, R. S.; Picoli, S., Jr.; de Vasconcelos, E. A.; da Silva, E. F., Jr. *An improved description of the dielectric breakdown in oxides based on a generalized Weibull distribution*. **2005**, 5.

Dissado, L.A.; Fothergill, J.C. Electrical Degradation and Breakdown in Polymers. Peter Peregrinus Ltd., London. **1992.** 319-355.

Fontanella, J.J.; Bendler, J.T.; Schuele D.E.; Edmondson, C.A.; Lomax, J.F. *Effect of pressure on the water relaxation in Ultem® polyetherimide*. Accepted to *Journal of Non-Crystalline Structures* **Nov 11 2006**, 6.

Fontanella, J.J.; McLin, M.G.; Wintersgill, M.C. *Journal of Polymer Science* **1994**, 32, 501.

Fothergill, J.C.. *IEEE Transaction on Electrical Insulation*, **June 1990**, 4, 489.

GE™ Plastics. "Ultem® Resin." http://www.geplastics.com/gep/Plastics/en/ ProductsAndServices/ProductLine/ultem.html

Guide for the statistical analysis of voltage endurance data for electrical insulation. ANSI/IEEE Std. 930-1987. **1987.**

Irene, Eugene A. Electronic Materials Science. Wiley, Hoboken, New Jersey. **2005**.

Leitch, Philip. http://en.wikipedia.org/wiki/Image:Weibull_CDF_2.PNG

Mueller, Joshua Michael. *Complex Impedance Studies of Electrosprayed and Extruded   Nafion Membranes*. Trident Scholar Project Report #324. 2004.

Ohanion, Hans C.; Markert, John T. Physics for Engineers and Scientists 3rd Ed. W.W.

Norton & Company, New York. **2007**.

Roy, M.; Nelson, J.K.; MacCrone, R.K.; Schadler, L.S.; Reed, C.W.; Keefe, R.; Zenger, W. *IEEE Transactions on Dielectrics and Electrical Insulation*. **August 2005**, 15, 629.

Theoleyre, S.; Reed, C.W. *Dielectric Properties of Polyetherimide Films*. **1984**, 5.

Weibull, W. *A statistical distribution function of wide applicability.* J. Appl. Mech.-Trans. ASME 18(3), 293-297. **1951.**

VIII. Glossary

amorphous – a material in which there is no long range order of the atoms

capacitance – the measure of the electric charge stored for a given potential applied to a capacitor

capacitor – electrical device that can store energy, modeled as two parallel conductive plates

conductivity – the ability of a material to conduct electrical current

crystallinity – a measure of the long range order within a material

defect – imperfection within the material, either a break in the bonds or a foreign substance that

> reduces the electric properties of the material

dielectric – an electrical insulator, resistant to current flow, often placed between the conductive

> plates of a capacitor

dielectric constant – the ratio of the permittivity of a material to that of free space, a measure of

> the degree of electric polarization of the material

dielectric loss – energy losses in a dielectric due to a dipole relaxation or conductivity within a

> material

dielectric strength – the maximum electric field a material can withstand before it breaks down

> and conducts electricity

dipole – a separation between positive and negative charge

electrode – conductor used to make electrical contact with a circuit

electron affinity – energy released when a neutral atom combines with an electron

glass transition temperature (T_g) – temperature below which an amorphous polymer is more

> rigid and above which the material is more plastic

histogram – graphical display of frequency of occurrence

ionization potential – energy require to remove an electron from an atom

K – degrees Kelvin, temperature scale where 0K is absolute zero and 273.15K is the freezing

    point for water

mil – one thousandth of an inch

nanoparticles – a particle with one dimension less than one hundred nanometers

silica – particles made of silicon dioxide

polarize – when dipoles within a dielectric rotated to align with an applied field

polymer – a large organic material made up of a repeated number of structural units (monomers)

potential (energy) – the negative of the work done by a conservative force, is this case the

    electrical force

relaxation process – the method by which a dipole gives up energy and aligns with an applied

    field

substrate – supporting foundation upon which a material is applied

voltage – the difference of electrical potential between two points on circuit, a measure of the

    potential energy per unit charge